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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/EP97/04749 <b>(22) International Filing Date:</b> 19 August 1997 (19.08.97) <b>(30) Priority Data:</b> 9618875.0                      10 September 1996 (10.09.96)    GB <b>(71) Applicant (for AU BB CA GB GH IE IL KE LC LK LS MN MW NZ SD SG SL SZ TT UG ZW only):</b> UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB). <b>(71) Applicant (for all designated States except AU BB CA GB GH IE IL KE LC LK LS MN MW NZ SD SG SL SZ TT UG ZW):</b> UNILEVER N.V. [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL). <b>(72) Inventors:</b> EUSER, Huug; Sportlaan 76, NL-3135 GW Vlaardingen (NL). WAGNER, Henning; Baanstraat 17, NL-3111 KM Schiedam (NL). APPEL, Peter, Willem; Prinses Julianalaan 79, NL-3062 DC Rotterdam (NL). <b>(74) Agent:</b> MOLE, Peter, Geoffrey; Unilever plc, Patent Division, Colworth House, Sharnbrook, Bedford MK44 1LQ (GB).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.          Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> PROCESS FOR PREPARING HIGH BULK DENSITY DETERGENT COMPOSITIONS <b>(57) Abstract</b> <p>A process for preparing a granular detergent composition comprises a first step of preparing a liquid component comprising a structurant. A second step comprises admixture of the liquid with a solid component in a granulator. An optional third step comprises drying and/or cooling. The structurant is incorporated in an amount such that the liquid component is pumpable at temperatures of 50 °C or more but causes sufficient solidification to form a free-flowing granulated product.</p>		

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PROCESS FOR PREPARING HIGH BULK DENSITY DETERGENT  
COMPOSITIONS

FIELD OF THE INVENTION

5

The present invention relates to a process for preparing a granular detergent composition or component by mixing. More in particular, it relates to a process for the continuous preparation of such detergent compositions.

10 Furthermore, it relates to a granular detergent composition obtainable by the process of the present invention.

BACKGROUND OF THE INVENTION

15

Generally speaking, there are two main types of processes by which detergent powders can be prepared. The first type of process involves spray-drying and aqueous detergent slurry in a spray-drying tower. In the second type of process the various components are dry-mixed and optionally agglomerated with liquids, e.g. nonionics. The latter kind of process is more suited to the production of powders having a relatively high bulk density. That is primarily because the chemical composition of the slurry used in the spray drying process markedly affects the bulk density of the granular product. This bulk density can only be significantly increased by increasing the content of relatively dense sodium sulphate. However, sodium sulphate does not contribute to detergency, so that the overall performance of the powder in the wash is thereby reduced.

30

In the past few years, there have been several proposals for mechanical mixing processes for the production of high density detergent powders. For example EP-A-265 203 discloses liquid surfactant compositions which contain a sodium or potassium salt of an alkylbenzene sulphonate or alkyl sulphate, an ethoxylated nonionic surfactant and

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water. The amount of water does not exceed 10% by weight. Such liquid surfactant composition may be sprayed onto a solid particulate absorbent material, for instance a porous spray-dried base powder having a low bulk density and  
5 containing little or no actives, to form a detergent base powder having an increased bulk density.

EP-A-507 402 discloses a process for preparing a liquid surfactant composition comprising an anionic surfactant, a nonionic surfactant and having a relatively low water  
10 content. The principle of the process is to neutralize the acid corresponding to the anionic surfactant with a neutralizing agent of a strength such as to lead to the desired low level of water in the final product by adding these two materials to a fluid which comprises the nonionic  
15 surfactant and which acts as a solvent or diluent for the neutralized anionic surfactant. This process is carried out continuously, preferably in a loop reactor.

EP-A-420 317 discloses a process for the continuous preparation of granular detergent compositions or components  
20 having a higher density than is achievable in spray drying processes. The process consists of three steps, an agglomeration in a high-speed mixer, a densification in a moderate-speed granulator densifier whereby the material is brought or maintained in a deformable state, and the drying  
25 and/or cooling of the product (e.g. in a fluid bed). A liquid acid precursor of an anionic surfactant is in situ neutralized by a solid water-soluble alkaline inorganic material (e.g. sodium carbonate) in the high-speed mixer. The deformable state of the material at temperatures above  
30 40°C is obtained at least partially by the heat of neutralization of the acid.

EP-A-544 365 discloses a process for the preparation of a granular composition in the same equipment described in EP  
0 420 317 or alternative in a batch granulation. In this  
35 case a mixture of a sodium or potassium salt of an alkyl

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sulphate e.g. a primary alkyl sulphate and an alkyoxylated nonionic surfactant is used as the liquid phase for the granulation in the high speed mixer. For obtaining detergent powders with good powder properties the agglomeration process is controlled by a significant increase of the liquid viscosity. This is obtained by the addition of one or more components to the liquid surfactant composition. Examples of such viscosity raising components are water and fatty acid in combination with stoichiometric amount of alkaline material (e.g. caustic soda) sufficient to neutralize the fatty acid which results in the formation of soap.

When the powder is to be formulated to contain a phosphate detergency builder such as sodium tripolyphosphate, the known mixing processes have a number of drawbacks which are deleterious to the requirement to produce free-flowing powders with good granularity and low moisture content. These in part are probably attributable to the low liquid carrying capacity of the phosphate builder particles. Typical problems which can be encountered include the build-up of hard lumps due to brisk exothermic hydration and crystal bridge formation. Moreover, soft granules tend to be formed in the resultant product with poor powder behaviour due to the low adhesive forces of the wet particle surfaces and hence, poor granule structure.

A. Naviglio and A. Moriconi ("Detergents Manufacture - A new, low cost, energy-saving, cool and dry process", Soap/Cosmetics/Chemical Specialities, Sept. 1987) describe a continuous process with a turbo reactor and a rotating drum agglomerator for the preparation of granular detergent compositions. The dry neutralisation reaction takes place in the turbo reactor into which the solids are dosed at the same time (e.g. solids: STP, alkaline powder (e.g. sodium carbonate); liquids: caustic solution, LAS acid, fatty acid). The mixing in the turbo reactor is achieved by

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special air diffusers which keep the powders and the liquids suspended. Cooled air is used to eliminate the reaction heat. The reactor contains a screw for continuous conveying to the agglomeration step. The agglomeration is provided by spraying on sodium silicate or nonionics in the rotating drum. This process provides a separation of the neutralisation/hydration and the agglomeration. Formation of large lumps of hydrated STP might be prevented by the suspension with an air stream. Due to the low absorption capacity of STP the spraying on of nonionics is not suitable for preparing detergent powders with a high content of actives.

#### SUMMARY OF THE INVENTION

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The problems related to the inclusion of STP or other solids having a low liquid-carrying capacity and/or hydratable properties have, however, now been overcome by a new but simpler process which can be effected using reactor and mixer equipment which is already conventional in the art. However, it also has advantages in the processing of other kinds of solids. This new process constitutes the present invention and formulating a liquid component with a structurant so as to remain pumpable at the temperature at which the liquid component is formed and then admixing it with a solid component at a lower temperature at which the structurant causes solidification of the mixture.

International Patent Specification No. 95/32276 discloses a process in which "liquid" components are formulated as a (preferably aqueous) paste having a viscosity of between 5 and 100 Pas at 70°C and then granulated with a solid component. However, this process does not disclose use with phosphate builders or other inorganic salts with similar liquid carrying and/or hydration properties and so the problems solved by the



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present invention are not addressed. Moreover, it does not provide the convenience of being able to pump the liquid component and the solution to providing low relative humidity products is also not addressed. For example, the process of the present invention also produces unexpected benefits with different detergency builders such as zeolites, enabling the manufacture of granular products with a lower relative humidity without drying than hitherto. This low humidity allows percarbonate bleaches to be post dosed, these being preferred over perborates on environmental grounds.

The resultant granulated product which when tabletted, produces tablets having a high degree of hardness as measured by break strength ( $P_{max}$ ) and E modulus ( $E_{mod}$ ). These parameters can optionally be used also to characterise the solidified blend in the granulator.

Thus, in a first aspect, the present invention provides a process for preparing a granular detergent composition, the process comprising a first step of preparing a liquid component which comprises a structurant, a second step of admixture of the liquid component with a solid component in a granulator and optionally, a third drying and/or cooling step, the structurant being incorporated in an amount such that the liquid component is pumpable at temperatures of 50°C or more (e.g. 60°C or more) but causes sufficient solidification during the second and/or third steps to form a free-flowing granulated product.

In a second aspect, the invention provides a granular detergent composition or component prepared by this process.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The granular product so prepared can be considered to be free flowing if it has a dynamic flow rate (DFR) of preferably more than 90ml/s. Conveniently, DFR can be

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measured by a technique whereby known volume of powder is permitted to flow through a calibrated orifice and tube. The flow time between two light sensors is automatically recorded and the DFR is calculated with the known volume and the recorded flow time.

Granular detergent compositions according to the present invention may be in the form of complete products ready for sale to the consumer. Alternatively, they may be formulated as base powders or adjuncts for admixture with other ingredients. In any event such compositions may have a bulk density of 550 g/l, more preferably at least 650 g/l. However, these products may also be produced with lower bulk densities.

Preferred embodiments of process and compositions according to the present invention may be characterised by the strength and E-modulus of a sample of

- (a) tabletted composition produced by the process; and/or
- (b) tablet formed by cooling of the liquid component until it solidifies.

The strength (hardness) measurement can be obtained using an Instron pressure apparatus. The powder is tabletted in a punch and die to form a tablet 9 mm in diameter and 16 mm in height, formed by exerting a maximum pressure of 10 tons on the tablet surface. In the case of a solidified liquid component taken from the process before it contacts the solid component, the tablet diameter is 14 mm and its height is 19 mm.

The tablet (powder or liquid component) is destroyed between a fixed and a moving plate. The speed of the moving plate is set to 5 mm/min, which causes a measuring time of about 2 sec. The pressure curve is logged on a computer. Thus, the maximum pressure (at the moment of tablet breaking) is given and the E-modulus is calculated from the slope.

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For the granular product, the minimum value of  $P_{max}$  is preferably 0.5 M Pa, most preferably 2 M Pa and the minimum value of  $E_{mod}$  is preferably 20 M Pa, most preferably 50 M Pa. However, for the solidified liquid component,  $P_{max}$  at 20°C is  
5 preferably a minimum of 0.2 M Pa, e.g. from 0.3 to 0.5 M Pa. At 55°C, a typical range is from 0.05 to 0.25 M Pa. At 20°C,  $E_{mod}$  for the blend is preferably a minimum of 3 M Pa, e.g. from 5 to 10 M Pa.

The liquid component is preferably prepared in a shear  
10 dynamic mixer for premixing the components thereof and performing any neutralisation of anionic acid precursor. The dynamic mixer is preferably located in a loop with a heat exchange to remove the heat of reaction of such neutralisation.

15 In the context of the present invention, the term "structurant" means any component which enables the liquid component to achieve solidification in the granulator and hence good granulation, even if the solid component has a low liquid carrying capacity.

20 Structurants may be categorised as those believed to exert their structuring (solidifying) effect by one of the following mechanisms, namely: recrystallisation (e.g. silicate or phosphates); creation of a network of finely divided solid particles (e.g. silicas or clays); and those  
25 which exert steric effects at the molecular level (e.g. soaps or polymers) such as those types commonly used as detergency builders. One or more structurants may be used.

Soaps represent one preferred class of structurant, especially when the liquid component comprises a liquid  
30 nonionic surfactant. In many cases it may be desirable for the soap to have an average chain length greater than the average chain length of the liquid nonionic surfactant but less than twice the average chain length of the latter.

If desired, solid components may be dissolved or  
35 dispersed in the liquid component. Typical amounts of the

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essential components of the ingredients of the liquid phase are as follows.

Preferably from 10% to 98% by weight of the substantially liquid component comprises liquid nonionic surfactant, more preferably from 30% to 70% by weight and especially from 40% to 50% by weight; and preferably from 98% to 10 by weight of the anionic surfactant, more preferably from 70% to 30% and especially from 50% to 40% by weight. The total amount of structurant is preferably from 2% to 30% by weight of the liquid component, more preferably from 5% to 20% or 5% to 15% by weight and especially from 10% to 15% by weight. It is generally preferred (although not absolutely mandatory) for the liquid component to comprise at least some liquid nonionic surfactant. However, in general, other organic solvents may be used instead of or in addition to the liquid nonionic.

The liquid component is also preferably substantially non-aqueous. That is to say, the total amount of water therein is not more than 15% by weight of the liquid phase, preferably not more than 10% by weight, typically from 5% to 8%, especially from 6% to 7%.

Typically, from 3% to 4% by weight of the liquid component may be water as the reaction by-product and the rest of the water present will be the solvent in which the alkaline material was dissolved. The liquid phase is very preferably devoid of all water other than that from the latter-mentioned sources, except perhaps for trace amounts/impurities.

It is very much preferred to form some or all of any anionic surfactant in situ in the liquid component by reaction of an appropriate acid precursor and an alkaline material such as an alkali metal hydroxide, e.g. NaOH. Since the latter normally must be dosed as an aqueous solution, that inevitably incorporates some water.

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Moreover, the reaction of an alkali metal hydroxide and acid precursor also yields some water as a by-product.

However, in principle, any alkaline inorganic material can be used for the neutralisation but water-soluble  
5 alkaline inorganic materials are preferred. Another preferred material is sodium carbonate, alone or in combination with one or more other water-soluble inorganic materials, for example, sodium bicarbonate or silicate. As alluded to above, sodium carbonate can provide the necessary  
10 alkalinity for the wash process, but it can additionally serve as a detergency builder. In this case the invention may be advantageously used for the preparation of detergent powders in which sodium carbonate is the sole or principal builder. Then, substantially more carbonate will be present  
15 than required for the neutralization reaction with the acid anionic surfactant precursor.

The liquid component may optionally comprise dissolved solids and/or finely divided solids which are dispersed therein. The only limitation is that with or without  
20 dissolved or dispersed solids, the liquid component should be pumpable at temperatures of 50°C or greater or at any rate, 60°C or greater e.g. 75°C. Preferably it is solid at below 50°C, preferably at 25°C or less. Generally speaking, pumpable liquid components have a viscosity no greater than  
25 1 Pa at the shear rate of the pumping. The structurants cause solidification in the blender preferably to produce blend and tablet strength as described hereinbefore. Typically, the temperature in the granulation is more than 10°C, preferably more than 20°C below the temperature at  
30 which the blend is prepared and pumped into the granulator.

If the solid component comprises or substantially consists of a phosphate builder the weight ratio of liquid component to the solid component when the two are brought into contact for mixing is from 0.25:1 to 0.5:1. If the  
35 solid component comprises or substantially consists of an

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aluminosilicate builder, this ratio is preferably from 0.4:1 to 0.7:1.

Suitable anionic surfactants are well-known to those skilled in the art. Examples suitable for incorporation in the liquid phase include alkylbenzene sulphonates, particularly linear alkylbenzene sulphonates having an alkyl chain length of C8-C15; primary and secondary alkyl sulphates, particularly C12-C15 primary alkyl sulphates; alkyl ether sulphates; olefin sulphonates; alkyl xylene sulphonates; dialkyl sulphosuccinates; and fatty acid ester sulphonates. Sodium salts are generally preferred.

The nonionic surfactant component of the liquid phase may be any one or more liquid nonionics selected from primary and secondary alcohol ethoxylates, especially C<sub>8</sub>-C<sub>20</sub> aliphatic alcohols ethoxylated with an average of from 1 to 20 moles ethylene oxide per mole of alcohol, and more especially the C<sub>10</sub>-C<sub>15</sub> primary and secondary aliphatic alcohols ethoxylated with an average of from 1 to 10 moles of ethylene oxide per mole of alcohol. Non-ethoxylated nonionic surfactants include alkylpolyglycosides, glycerol monoethers, and polyhydroxyamides (glucamide).

The liquid acid precursor may be selected from linear alkyl benzene sulphonic acids, alphaolefin sulphonic acids, internal olefin sulphonic acids, fatty acid ester sulphonic acids and combinations thereof. The process of the invention is especially useful for producing compositions comprising alkyl benzene sulphonates by reaction of the corresponding alkyl benzene sulphonic acid, for instance Dobanoic acid ex Shell.

Linear or branched primary alkyl sulphates having 10 to 15 carbon atoms can also be used.

The solid component with which the liquid phase is admixed preferably comprises a detergency builder. The total amount of detergency builder in the final compositions is suitably from 10 to 80 wt%, preferably from 15 to 60 wt%.

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The builder may be present in an adjunct with other components or, if desired, separate builder particles containing one or more builder materials may be employed.

The present invention is especially applicable to use  
5 where the solid component comprises hydratable salts, preferably in substantial amounts such as at least 25% by weight of the solid component, preferably at least 10% by weight. Hydratable solids include inorganic sulphates and carbonates, as well as inorganic phosphate builders, for  
10 example, sodium orthophosphate, pyrophosphate and tripolyphosphate,

Other suitable builders include crystalline and amorphous aluminosilicates, for example zeolites as disclosed in GB-A-1 473 201; amorphous aluminosilicates as  
15 disclosed in GB-A-1 473 202; and mixed crystalline/amorphous aluminosilicates as disclosed in GB 1 470 250; and layered silicates as disclosed in EP-B-164 514.

Aluminosilicates, may suitably be present in a total amount of from 10 to 60 wt% and preferably an amount of from  
20 15 to 50 wt%. The zeolite used in most commercial particulate detergent compositions is zeolite A. Advantageously, however, maximum aluminium zeolite P (zeolite MAP) described and claimed in EP-A-384 070 may be used. Zeolite MAP is an alkali metal aluminosilicated of  
25 the P type having a silicon to aluminium ratio not exceeding 1.33, preferably not exceeding 1.15, and more preferably not exceeding 1.07.

Other inorganic builders that may be present include sodium carbonate (as mentioned above, an example of a  
30 hydratable solid), if desired in combination with a crystallisation seed for calcium carbonate as disclosed in GB-A-1 437 950. As mentioned above, such sodium carbonate may be the residue of an inorganic alkaline neutralising agent used to form a nonionic structurant in situ.

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Organic builders that may be present include polycarboxylate polymers such as polyacrylates, acrylic/maleic copolymers, and acrylic phosphinates; monomeric polycarboxylates such as citrates, gluconates, oxydisuccinates, glycerol mono-, di- and trisuccinates, carboxymethyloxysuccinates, carboxymethyloxymalonates, dipicolinates, hydroxyethyliminodiacetates, aminopolycarboxylates such as nitrilotriacetates (NTA), ethylenediaminetetraacetate (EDTA) and iminodiacetates, alkyl- and alkenylmalonates and succinates; and sulphonated fatty acid salts. A copolymer of maleic acid, acrylic acid and vinyl acetate is especially preferred as it is biodegradable and thus environmentally desirable. This list is not intended to be exhaustive.

Especially preferred organic builders are citrates, suitably used in amounts of from 5 to 30 wt%, preferably from 10 to 25 wt%; and acrylic polymers, more especially acrylic/maleic copolymers, suitably used in amounts of from 0.5 to 15 wt%, preferably from 1 to 10 wt%. The builder is preferably present in alkali metal salt, especially sodium salt, form.

Granular detergent compositions of the invention may contain, in addition to the nonionic and ionic surfactants of the liquid blend, one or more other detergent-active compounds (surfactants) which may be chosen from soap and non-soap anionic cationic, nonionic, amphoteric and zwitterionic detergent-active compounds, and mixtures thereof. These may be dosed at any appropriate stage before or during the process. Many suitable detergent-active compounds are available and are fully described in the literature, for example, in "Surface-Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch. The preferred detergent-active compounds that can be used are soaps and synthetic non-soap anionic and nonionic compounds.



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Detergent compositions according to the invention may also contain a bleach system, desirably a peroxy bleach compound, for example, an inorganic persalt or organic peroxyacid, capable of yielding hydrogen peroxide in aqueous solution. The peroxy bleach compound may be used in conjunction with a bleach activator (bleach precursor) to improve bleaching action at low wash temperatures. An especially preferred bleach system comprises a peroxy bleach compound (preferably sodium percarbonate optionally together with a bleach activator), and a transition metal bleach catalyst as described and claimed in EP 458 397A and EP-A-509 787.

Usually, any bleach and other sensitive ingredients such as enzymes and perfumes will be post-dosed after granulation as will be minor ingredients.

Typical minor ingredients include sodium silicate; corrosion inhibitors including silicates; antiredeposition agents such as cellulosic polymers; fluorescers; inorganic salts such as sodium sulphate, lather control agents or lather boosters as appropriate; proteolytic and lipolytic enzymes; dyes; coloured speckles; perfumes; foam controllers; and fabric softening compounds. This list is not intended to be exhaustive.

Powder flow may be improved by the incorporation of a small amount of an additional powder structurant, for example, a fatty acid (or fatty acid soap), a sugar, an acrylate or acrylate/maleate polymer, or sodium silicate which is suitably present in an amount of from 1 to 5 wt%.

Regarding the equipment used for the mixing stage(s) of the process (i.e. after admixture of the liquid and solid components), the liquid component is preferably admixed with the solid components in a first mixing step in a high-speed mixer/densifier to form a granular detergent material. Optionally, the granular detergent material from the first mixing step may subsequently be treated in a second mixing

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step in a moderate-speed granulator/densifier. If high bulk density product is desired, at this stage it can be brought into or maintained in the required deformable state. In any event, the product of the first mixing step or the second  
5 mixing step may then be cooled and/or dried.

The residence time in the high-speed mixer/densifier in the first mixing step is preferably from about 5 to 30 seconds. The residence time in the moderate-speed mixer/densifier during any second (optional) mixing step is  
10 preferably from about 1 to 10 minutes. It is preferred to perform any such process as a continuous process but it could be performed as a batch process in a high shear or low shear mode.

In the first mixing step, the solid components of the  
15 feedstock are very thoroughly mixed with the liquid blend by means of a high-speed mixer/densifier. Such a mixer provides a high energy stirring input and achieves thorough mixing in a very short time.

As high-speed mixer/densifier we advantageously used  
20 the Lödige (Trade Mark) CB 30 Recycler. This apparatus essentially consists of a large, static hollow cylinder having a diameter of about 30 cm which is horizontally placed. In the middle, it has a rotating shaft with several different types of blades mounted thereon. It can be  
25 rotated at speeds between 100 and 2500 rpm, dependent on the degree of densification and the particle size desired. The blades on the shaft provide a thorough mixing action of the solids and the liquids which may be admixed at this stage. The mean residence time is somewhat dependent on the  
30 rotational speed of the shaft, the position of the blades and the weir at the exit opening.

Other types of high-speed mixers/densifiers having a comparable effect on detergent powders can also be contemplated. For instance, a Shugi (Trade Mark) Granulator  
35 or a Drais (Trade Mark) K-TTP 80 may be used.

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In the first mixing step, the components of the feedstock are thoroughly mixed in a high-speed mixer/densifier for a relatively short time of about 5-30 seconds, preferably under conditions whereby the starting material is brought into, or maintained in, a deformable state, to be defined hereafter.

In the case of production of high bulk density products, after the first mixing step, if the resultant detergent material still possesses a considerable porosity, then instead of choosing a longer residence time in the high-speed mixer/densifier to obtain a further bulk density increase, it may then be subjected to the optional second mixing step in which the detergent material is treated for 1-10 minutes, preferably for 2-5 minutes, in a moderate-speed granulator/densifier. During this second processing step, the conditions are such that the powder is brought into, or maintained in, a deformable state. As a consequence, the particle porosity will be further reduced. The main differences with the first step reside in the lower mixing speed and the longer residence time of 1-10 minutes, and the necessity for the powder to be deformable.

The optional second mixing step can be successfully carried out in a Lödige (Trade Mark) KM 300 mixer, also referred to as Lödige Ploughshare. This apparatus essentially consists of a hollow static cylinder having a rotating shaft in the middle. On this shaft various plough-shaped blades are mounted. It can be rotated at a speed of 40-160 rpm. Optionally, one or more high-speed cutters can be used to prevent excessive agglomeration. Another suitable machine for this step is, for example the Drais (Trade Mark) K-T 160.

However, instead of using a high-speed mixer densifier machine, followed by a separate moderate speed-mixer densifier machine, the same effect could be obtained using a single machine operated at two speeds. It could be operated

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first at high speed for mixing/densification and then at moderate speed for granulation/densification. Suitable machines include mixers of the Fukae<sup>®</sup> FS-G series; Diosna<sup>®</sup> V series ex Dierks & Sohne, Germany; Pharma Matrix<sup>®</sup> ex T.K. Fielder Ltd; England; Fuji<sup>®</sup> VG-C series ex Fuji Sangyo Co., Japan; the Roto<sup>®</sup> ex Zanchetta & Co. srl, Italy and the Schugi<sup>®</sup> Flexomix granulator.

For use, handling and storage, the densified detergent powder must be in a free flowing state. Therefore, in a final step the powder can be dried and/or cooled if necessary. This step can be carried out in a known manner, for instance in a fluid bed apparatus (drying, cooling) or in an airlift (cooling). It is advantageous if the powder needs a cooling step only, because the required equipment is relatively simple and more economical.

For production of high bulk density products, any optional second mixing step and preferably also for the first mixing step, the detergent powder should be brought into a deformable state in order to get optimal densification. The high-speed mixer/densifier and/or the moderate speed granulator/densifier are then able to effectively deform the particulate material in such a way that the particle porosity is considerably reduced or kept at a low level, and consequently the bulk density is increased.

The invention will now be explained in more detail by way of the following non-limiting examples.

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EXAMPLES1. Granulation of STP:

5 Preparation of the blend in the loop-reactor with

LAS acid: 69.4 kg/h

Premix Nonionic

surfactant/Fatty acid

Nonionic surfactant 7 EO 58.9 kg/h

Nonionic surfactant 3 EO 31.7 kg/h

Fatty acid C16-C18 17.7 kg/h

Neutralisation with caustic soda to pH 11:

NaOH-solution (50%): 22.3 kg/h

This blend (200 kg/h, water content = 10%) was used for the granulation of 600kg/h STP in the recycler (Loedige CB30).

10

2. Granulation of STP, Sulphate and Carbonate:

Preparation of the blend in a loop-reactor with

LAS acid: 74.7 kg/h

15 Neutralisation of the LAS acid with caustic soda:

NaOH-solution (50%): 18.4 kg/h

Alkaline silicate solution(45%): 38.1 kg/h

Neutralisation of the alkalinity with a premix of nonionic surfactant/fatty acid:

20 Nonionic surfactant 7 EO 63.3 kg/h

Nonionic surfactant 3 EO: 34.1 kg/h

Fatty acid C16-C18: 17.1 kg/h

This blend (245.6 kg/h, water content = 13.2%) was used for the granulation of the following powders in the recycler

25 (Loedige CB30):

STP: 700 kg/h

Sulphate: 350 kg/h

Carbonate: 100 kg/h

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In the light of this disclosure, modifications of the described examples, as well as other examples, all within the scope of the present invention as defined by the appended claims will now become apparent to persons skilled  
5 in the art.

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**CLAIMS:**

1. A process for preparing a granular detergent composition, the process comprising a first step of  
5 preparing a liquid component which comprises a structurant, a second step of admixture of the liquid component with a solid component in a granulator, and optionally, a third drying and/or cooling step, the structurant being incorporated in an amount such that the liquid component is  
10 pumpable at temperatures of 50°C or more but causes sufficient solidification during the second and/or third steps to form a free-flowing granulated product.
2. A process according to claim 1, wherein the liquid  
15 component is pumpable at a temperature of 60°C or more, preferably 75°C or more.
3. A process according to either preceding claim, wherein the liquid component is solid at preferably at below 50°C,  
20 preferably at 25°C or less.
4. A process according to any preceding claim, wherein the liquid component solidifies to form a tablet which at 20°C has a  $P_{max}$  value of at least 0.2 M Pa, preferably from 0.3 to  
25 0.5 M Pa and/or an  $E_{mod}$  value of at least 3 M Pa, preferably from 5 to 10 M Pa.
5. A process according to any preceding claim, wherein the liquid component is substantially non-aqueous.  
30
6. A process according to claim 5, wherein the liquid component contains no more than 15% by weight of water.
7. A process according to any preceding claim, wherein the  
35 granular detergent composition can be formed into a tablet

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having a  $P_{max}$  value of at least 0.5 M Pa and/or an  $E_{mod}$  value of at least 20 M Pa.

8. A process according to any preceding claim, wherein the  
5 solid component comprises a hydratable solid material.

9. A process according to any preceding claim, wherein the solid component comprises a detergency builder material.

10. A process according to claim 9, wherein the detergency builder material comprises a phosphate builder.

11. A process according to claim 9 or claim 10, wherein the detergency builder material comprises an aluminosilicate.

12. A process according to any preceding claim, wherein the liquid component further comprises a liquid nonionic surfactant.

13. A process according to claim 12, wherein liquid component contains from 10% to 98% by weight of that component of liquid nonionic surfactant.

14. A process according to any preceding claim, wherein the liquid component contains from 98% to 10% by weight of that component of anionic surfactant.

15. A process according to any preceding claim, wherein the liquid component contains up to 30% by weight of that component of structurant.

16. A process according to any preceding claim, wherein the weight ratio of the liquid component to the solid component is from 0.25:1 to 0.7:1.



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17. A granular detergent composition prepared by a process according to any preceding claim.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 97/04749

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 C11D17/06 C11D11/00 C11D11/04

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
X	EP 0 694 608 A (PROCTER & GAMBLE) 31 January 1996 see page 3, line 10 - page 5, line 45; claims 1-9; examples 1-16 ---	1-17
X	EP 0 663 439 A (PROCTER & GAMBLE) 19 July 1995 see page 3, line 19 - page 7, line 2; claims 1-14; examples 1-4 ---	1-17
X	EP 0 622 454 A (PROCTER & GAMBLE) 2 November 1994 see page 3, line 10 - page 5, line 45; claims 1-15; examples 1-10 --- -/--	1-17

☒ Further documents are listed in the continuation of box C

☒ Patent family members are listed in annex

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# INTERNATIONAL SEARCH REPORT

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